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CURRENT NOISE IN SODIUM β" ALUMINA CERAMIC

by

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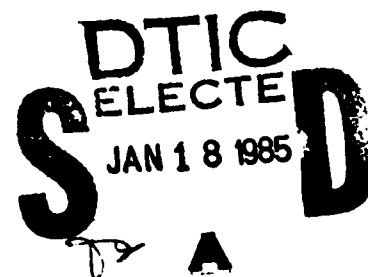
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ABSTRACT

Experimental bulk current noise spectra for Naβ'' alumina ceramics are observed over the frequency range $f=3\times10^{-3}$ Hz to 10^4 Hz and with low contact noise, amalgam electrodes. The noise is proportional to the square of the dc current and varies as $f^{-3/2}$, suggesting bulk conductivity fluctuations arising from diffusion of the conducting ions. The results indicate that individual grains in the ceramic are not stochastically independent and that only a small fraction of the conducting ions present participate in the diffusion noise process. The number of such ions is thermally activated with an activation energy of 0.75 eV. Chemical and electrochemical contact noise indicates a reaction at the ceramic-amalgam interface characterized by a reaction rate of $6.3\times10^2/\text{sec}^{-1}$, even for low-noise contacts.

I. INTRODUCTION

Electrical fluctuations accompanying dc current in Naβ" alumina and Agβ" alumina ceramics have previously been observed,[1,2] both at ohmic contacts and in the bulk. Experimental measurements are strongly influenced by contact noise effects, even in the absence of current, and by electrochemically induced changes in the noise power spectra. The present work examines bulk current noise in Naβ" alumina ceramics using improved experimental techniques that minimize both contact noise and electrochemical effects. Additionally, the spectral measurements are extended to 10^{-3}Hz and the effect of temperature on the noise level is determined.

II. EXPERIMENTAL TECHNIQUE

Commercial ceramic (90.4% Al_2O_3, 8.85% Na_2O, 0.75% Li_2O) samples[3], 1x1x0.4 cm, are provided with sodium amalgam current contacts and transverse potential electrodes by sealing the corners into the sides of four plastic test tubes with epoxy cement. One pair of diagonally opposing corner electrodes is used for current contacts and the other pair for transverse noise terminals. Contact to the amalgam electrodes is by means of platinum foil. All specimens are previously baked at 800°C in air for several hours and subsequently kept desiccated to reduce absorbed moisture. Experimental results

with this simple square configuration are not distinguishable from a cruciform shape (to reduce the possible influence of contact current noise on voltage fluctuations observed at the transverse contacts), nor from a square having four saw-cuts perpendicular to the sides, each extending approximately 1/3 of the sample width. Transverse noise voltages are independent of the value of a metallic resistance in series with the current contacts from 10^3 to 10^6 ohms (sample resistance 5×10^3 ohms), which indicates constant-current conditions.

Amalgam contacts are prepared by electrolytically depositing[4] Na from an 80% solution of NaCl using a current density of 0.1 A/cm^2 at 4 volts. A 2 mole percent amalgam can be produced in 10 cm^3 of Hg in about two hours. The amalgam is subsequently poured into the sample test tubes, yielding a contact area of 0.1 cm^2. The 2 mole percent value was selected as being sufficiently great to yield ohmic, low-noise contacts. Occasionally, samples are found to exhibit large contact noise effects in the absence of dc current, which is attributed to chemical reaction effects at the contacts.[2]

Voltage fluctuations at the transverse electrodes are observed with the contacts connected to the input of a PAR 113 preamplifier. The preamplifier output is analyzed digitally using an A/D conversion and FFT routine developed for the Apple IIe personal

computer.[5] The system accurately measures the Nyquist noise of resistances from 10^4 to $2x10^8$ ohm over the frequency range 10^{-4} to $2x10^4$ Hz. Current is supplied to the current terminals from a filtered battery source and through a 10^5 ohm series resistor.

III.   CONTACT NOISE

Typical contact noise spectra in the absence of current for pure Hg and approximately 0.1 mole percent amalgam electrodes, Fig. 1, are consistent with previous results[2] but are more detailed and exhibit lower noise levels. Both types of contacts show Nyquist noise associated with the sample resistance at high frequencies where the capacitive reactance of the blocking Hg contact is quite equivalent to the low resistance of the conducting amalgam contact and both are negligible compared to the bulk resistance.

Both spectra also show a relaxation noise at 100 Hz which has previously been seen only after net current flow.[2] The magnitude of this noise is reduced by mild abrasion of the sample contact surface while in contat with the amalgam and by allowing a virgin contact to age for several hours. This suggests that the effect is a chemical reaction noise at the sample/amalgam interface, which is analyzed in greater detail below.

The blocking Hg contact noise spectrum shows a second relaxation noise at 1 Hz which is not evident in the conducting contact data. The plateau is near the level of the Nyquist noise of the

$2x10^8$ ohm preamplifier input resistance and so the spectrum is viewed as the result of the preamplifier input resistance shunted by the capacitance of the series combination of the two blocking Hg contacts (since the sample resistance is negligible). The contact capacitance determined from the half-power frequency is $2.6x10^{-8}$ F/cm^2, and the effective separation of an equivalent parallel-plate capacitor is calculated to be about 300Å for a unity dielectric constant. Values as low as 10Å have been seen in other data, and are rather more representative.

Both contact materials have noise levels in excess of the $2x10^8$ ohm pre-amplifier input resistance Nyquist noise at frequencies below 10^{-1} Hz. This has been attributed to non-equilibrium chemical reaction noise[2]. It is unfortunate that even though the present data extends down to $3x10^{-3}$ Hz, no low-frequency plateau is observed which would permit some quantitative analysis. The contact noise levels in Fig. 1 are not as low as can be achieved with careful sample preparation, as considered later in connection with Fig. 3. In that case, contact noise is not observed above internal noise of the preamplifier.

IV.   CURRENT NOISE

Fig. 2 is representative of noise spectra observed in specimens having relatively low noise, 2 mole percent amalgam contacts.

The zero current transverse noise is similar to the amalgam contact noise in Fig. 1 except that the 100 Hz relaxation noise is absent. The low-frequency f^{-2} slope and the level in excess of preamplifier input resistance Nyquist noise below 10^{-1} Hz suggests residual chemical reaction noise, however.

The transverse noise level is considerably increased by current in the sample and the shape of the noise spectra is $f^{-1.6}$. This is in contrast to the contact current noise (that is, the noise at the current contacts in the presence of current), top curve in Fig. 2, which is orders of magnitude greater and has a spectral shape of $f^{-2.3}$. After transferring a charge of 1.8C through the sample, the transverse noise is observed to have increased significantly over initial results, as also illustrated in Fig. 2, and the spectral shape changes to f^{-2}. This may simply be the result of the very large contact current noise influencing measurements at the transverse contacts in spite of constant current conditions but due to slight sample asymmetry. Alternatively, if the change in transverse noise results from bulk electrochemical effects, the changes are not detectable above contact noise, for the zero current transverse noise spectra at the conclusion of these experiments is essentially identical to the initial I=0 data in Fig. 2.

In very low noise samples, contact noise is not observable above internal preamplifier noise as illustrated by the I=0 curve in Fig. 3. In this data, Nyquist sample noise exceeds amplifier noise above 20 Hz. The transverse current noise spectra all have a $f^{-1.5}$ dependence, in agreement with the initial transverse current noise spectra in Fig. 2, and the noise level is proportional to the square of the dc current. This specimen displayed stable and reproducible noise spectra for an extended time (8 hours) before beginning to show signs of instability such as associated with Fig. 2.

The temperature dependence of the transverse current noise in this sample is shown in Fig. 4. In the Nyquist noise regime (I=0 and f>10^3 Hz), the measured noise has an exponential dependence upon temperature with an activation energy of 0.3eV. This is in agreement with the temperature dependence of the resistivity of Naβ" alumina near room temperature[6] and again confirms observation of bulk sample Nyquist noise under these conditions. The temperature dependence of the current noise, at f=10 Hz and I=500 μA, is also observed to be exponential, but the activation energy is much greater, 1.2 eV.

V.   DISCUSSION

These experimental data show that current noise in Naβ" alumina ceramic has a $f^{-1.5}$ spectral shape in the absence of

disturbing contact noise and electrochemical effects. Noise voltages
at the transverse terminals can be interpreted in terms of bulk con-
ductivity fluctuations[7]. Furthermore, it is well established[8] that
diffusion in one, two, or three dimensions is characterized by a 3/2
power law. The voltage spectral density, $S(V,f)$, can be written as

$$\frac{S(V,f)}{V^2} = 4 \frac{<\Delta N^2>}{N^2} \left(\frac{D}{2L^2}\right)^{1/2} \omega^{-3/2} \tag{1}$$

where V is the dc voltage across the sample, $<\Delta N^2>$ and N are the
variance and average number of diffusing entities, D is the diffusion
constant, L is a characteristic length (see below), and ω is the
angular frequency. Eq. (1) is valid at frequencies greater than a
characteristic frequency, ω_0, where

$$\omega_0 = 2 \; D/L^2 \tag{2}$$

Below ω_0 the spectrum flattens, becoming a constant in the case of
three dimensional diffusion, or varying as $\omega^{-1/2}$ in one dimension.

A turnover frequency is not observed in the data of Fig. 3
down to 3×10^{-3} Hz, so a limit to the characteristic length may be
determined from Eq. (2). Taking $D=1.0\times10^{-6}$ cm^2/sec at room
temperature[6], the result is L>0.01 cm. This value is much larger
than the average grain size[9], 5×10^{-4} cm, which suggests individual

grains are not stochastically independent volumes. In view of this, it seems reasonable to assume that the characteristic length is essentially equal to the active sample length, approximately 1.0 cm.

Poisson statistics are commonly assumed[8], so that $<\Delta N^2> = N$ in Eq. (1). At a sample current of 250 μA, the voltage across the sample is 1.0 volt and the experimental data in Fig. 3 give $S(1V, 0.16Hz) = 7\times10^{-12}$ V^2/Hz. Inserting known values into Eq. (1), a value for N, the number of active diffusing ions, is calculated to be 4×10^8, or about 1×10^9 ions/cm^3. This is a much smaller number than the concentration of sodium ions known to be present, about 10^{22} ions/cm^3.

A possible explanation for this discrepancy may be found in the temperature dependence of the current noise. Writing the temperature dependence explicitly in Eq. (1),

$$S(V,f,T) = \frac{4I^2}{N} R^2(T) \left(\frac{D(T)}{2L^2}\right)^{1/2} \omega^{-3/2} \tag{3}$$

where R is the sample resistance, I is the current and T is the temperature. From the Einstein relation between the diffusion constant and conductivity, the temperature dependence of the resistance can be written as

$$D(T) = D_0 \exp(-E_d/kT)$$

$$R(T) = R_0 T \exp(E_d/kT)$$

where E_d is the activation energy for diffusion and k is Boltzmann's constant. Collecting the temperature dependent terms in Eq. (3),

$$S,(V,f,T) = S_0 R^2(T) D^{1/2}(T) = S_0 R_0^2 D_0^{1/2} T^2 \exp(3E_d/2kT) \quad (4)$$

The experimental value of the activation energy, 1.2eV, means that $E_d=0.8eV$, whereas the value of 0.3eV found from Nyquist noise is in agreement with literature values. Suppose, however, that t⊦   ⊓ber of ions responsible for diffusion noise is thermally act ⌐ed,

$$N = N_0 \exp(-E_n/kT) \quad (5)$$

then Eq. (4) becomes

$$S(V,f,T) = \frac{S_0' R_0^2 D_0^{1/2}}{N_0} T^2 \exp(3E_d/2+E_n)/kT$$

Taking $E_d = 0.3eV$, a value of $E_n = 0.75eV$ is determined. Inserting this and the room temperature value $N = 4 \times 10^8$ found previously into Eq. (5) yields $N_0 = 1.6 \times 10^{21}$ ions, or 4×10^{21} ions/cm^3. This is very close to the expected sodium concentration. The agreement is par-ticularly satisfactory in view of the several approximations introduced.

This analysis indicates that conductivity fluctuations in Na β'' alumina ceramic arise from diffusion of the conducting ions but that only a small fraction of the number of conducting ions present participate. The number of such active ions is thermally activated.

The results also lead to the somewhat surprising interpretation that the individual grains are not stochastically independent since the observed characteristic length is much greater than the average grain size.

The relaxation spectra at 100 Hz seen in contact noise may be treated in a similar fashion. In the simple case of a single reacting species characterized by a reaction rate k, the current and voltage fluctuations are given by[10]

$$\frac{S(V,f)}{V^2} = \frac{S(I,f)}{I^2} = \frac{4}{N}\frac{k}{k^2+\omega^2} \qquad (6)$$

where now V is the voltage across the contact region, I is the current arising from the number N of reacting surface ions, and Poisson statistics are assumed. In the absence of a faradaic current, I = kNe, where e is the electronic charge. Finally,

$$S(V,f) = \left(\frac{V}{I}\right)^2 S(I,f) = Z_c^2 S(I,f)$$

$$= \frac{4Nk^3e^2Z_c^2}{k^2+\omega^2} \qquad (7)$$

where Z_c is the effective impedance of the contact. From the turnover frequency observed in Fig. 1, f = 10^2 Hz, a value of k = 6.3×10^2 sec^{-1}

is determined. In the case of the blocking contact, Z_c is assumed to be dominated by the capacitance of the contact, found earlier to be 2.6×10^{-8} F/cm^2. Using the observed value of the noise voltage, $S(V,0) = 10^{-14}$V^2/Hz, the number of reacting species calculated from Eq. (7) is 1×10^8, or about 1×10^9 ions/cm^2. It has not been possible to further characterize the nature of this phenomenon other than to observe that surface abrasion changes the noise level and that the magnitude increases with current in the sample. This suggests a surface reaction that proceeds both chemically and electrochemically.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1.   Contact noise spectra of blocking mercury electrodes and
dilute sodium amalgam electrodes to Naβ" alumina ceramic.

Figure 2.   Transverse and longitudinal current noise spectra in
Naβ" alumina ceramic. The transverse noise at I=0 shows
chemical contact noise and the longitudinal noise
spectra (top curve) is current contact noise.
Transverse current noise changes from $f^{-1.6}$ to f^{-2} after
a charge of 1.8C from current in the sample.

Figure 3.   Transverse current noise in a Naβ" alumina ceramic
sample having very low noise contacts.

Figure 4.   Temperature dependence of Nyquist and bulk current noise
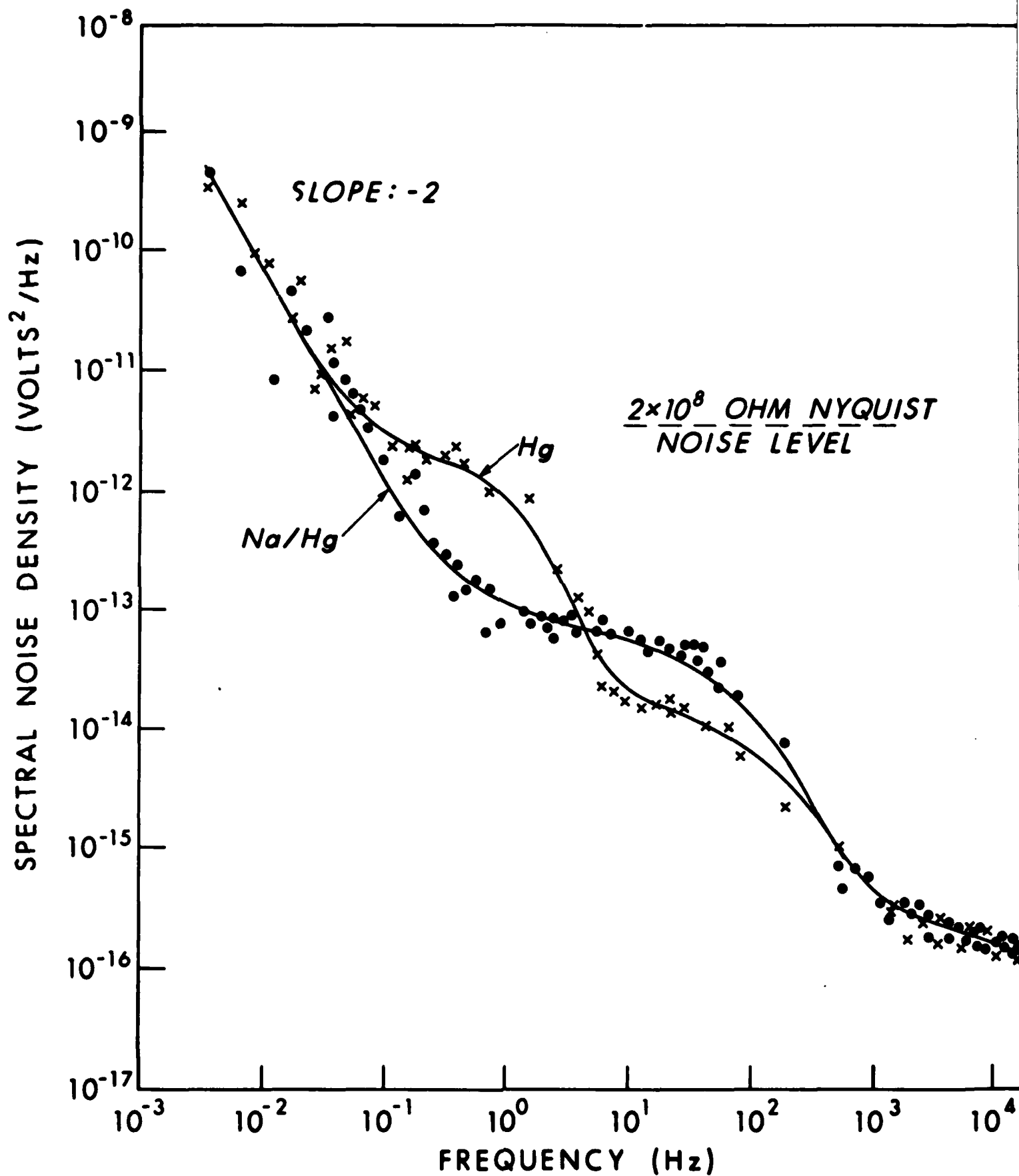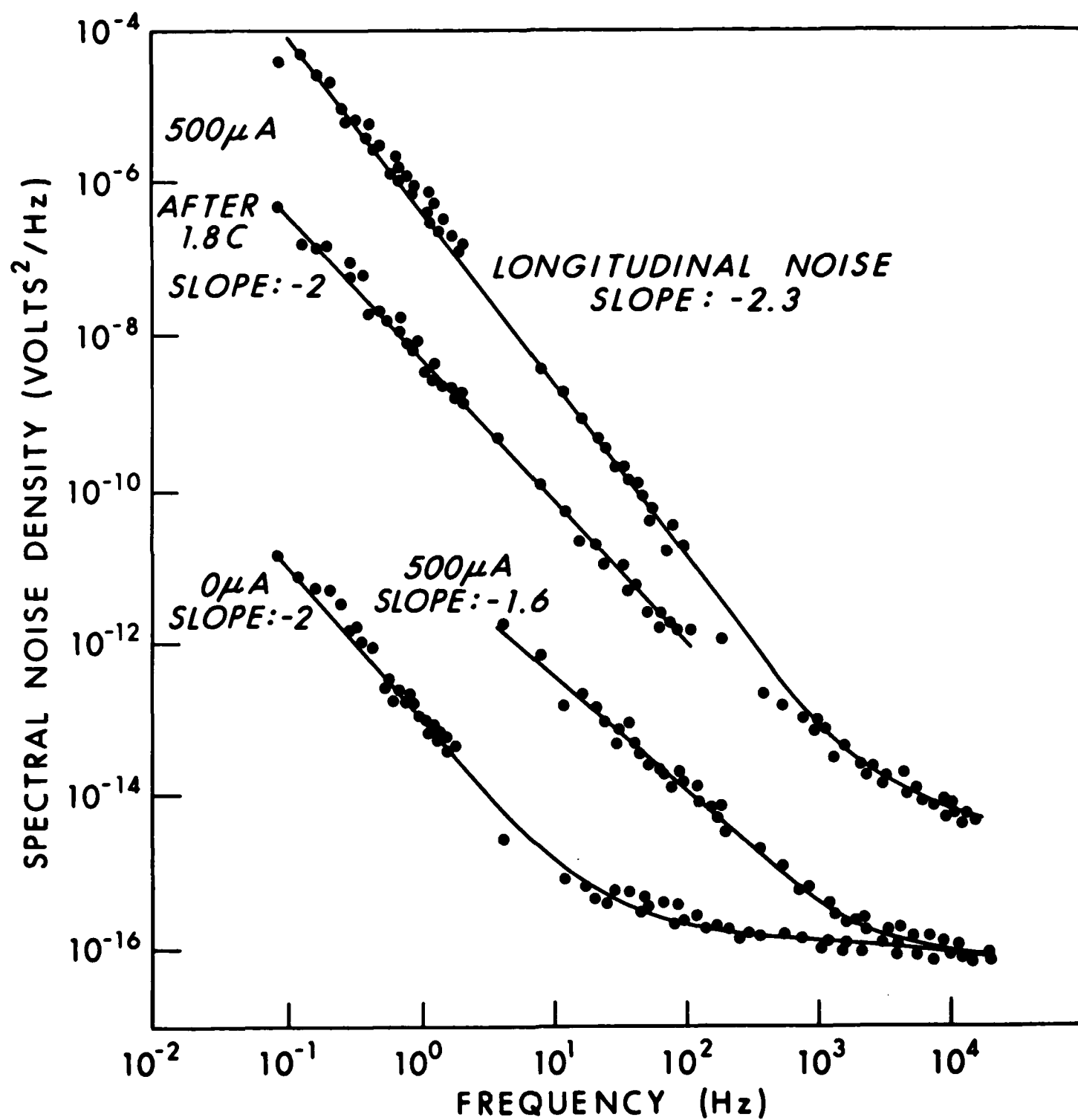of Naβ" alumina ceramic.

Figure 1

Figure 2

Figure 3
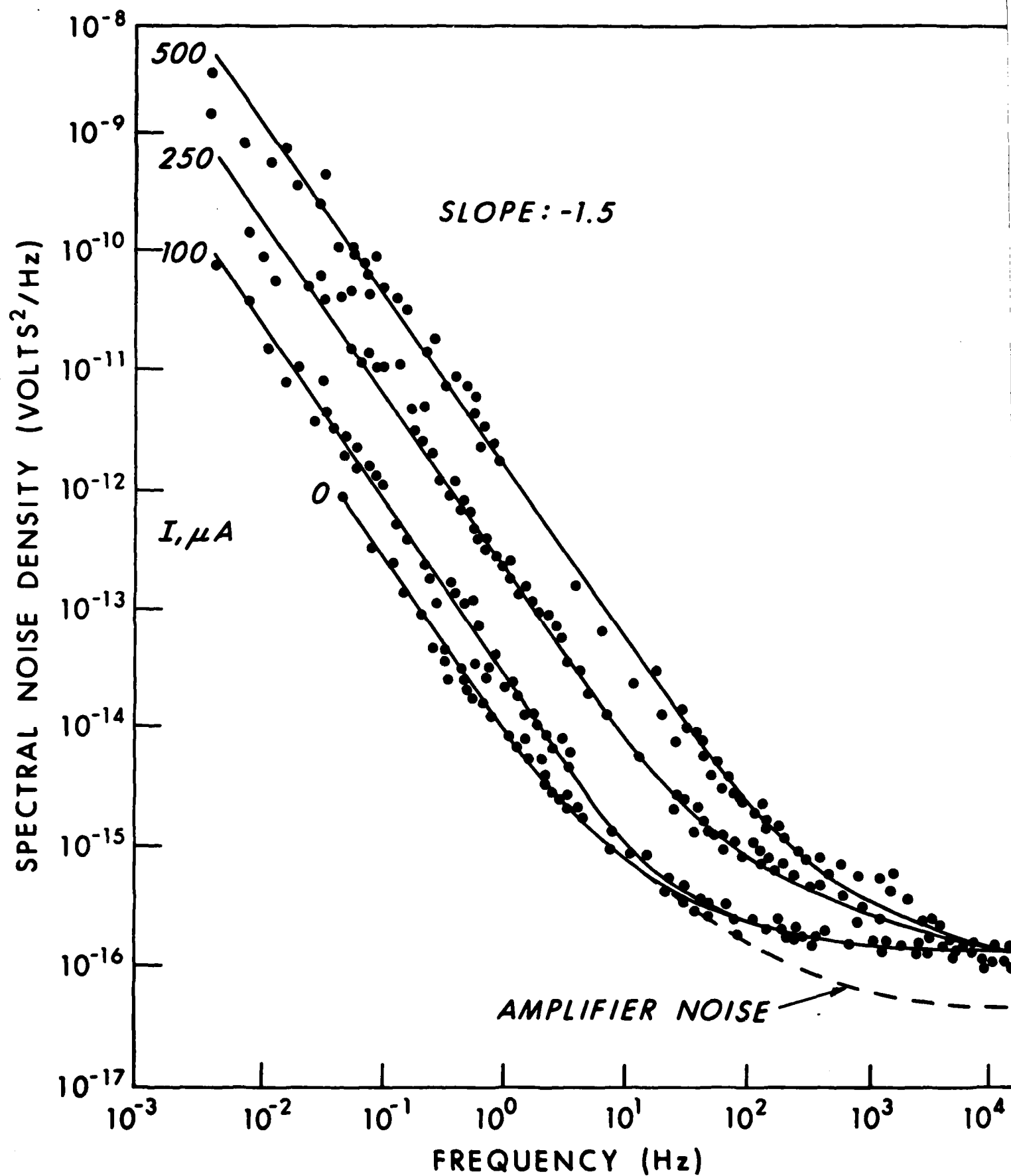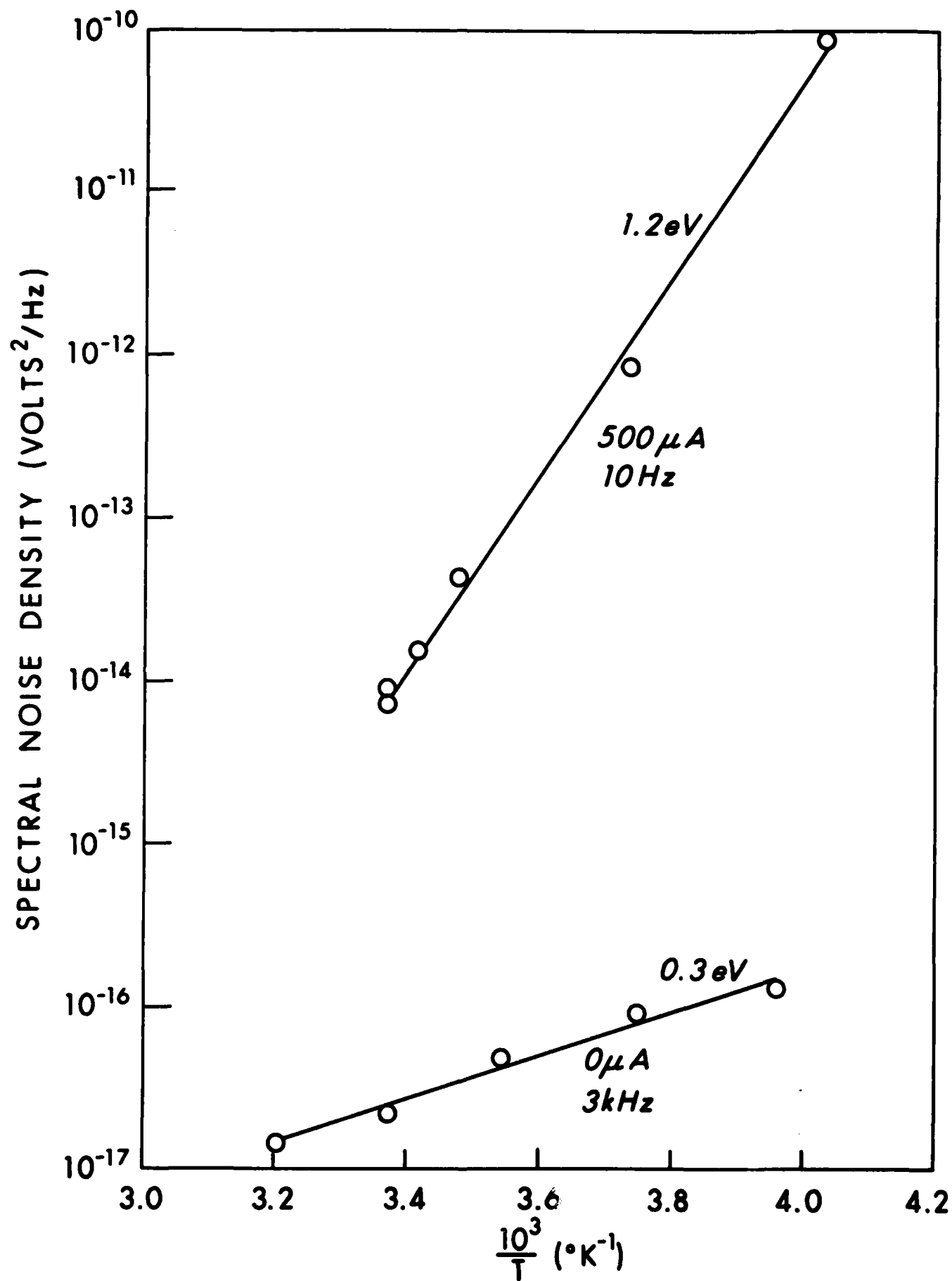
Figure 4

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